



Photoluminescence Studies of H₂O₂ Treated Chemically Synthesized ZnO Nanostructures

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Abstract

Spherical ZnO nanoparticles dispersed in PVA matrix were synthesised through chemical bath deposition method. The HRTEM images confirm the formation of wurtzite ZnO quantum dots. The PL spectra obtained were deconvoluted in order to study the defects due to impurities. Peak positions obtained through de-convolution exhibit the energy levels in the long wavelength regions. The defects such as oxygen vacancy, oxygen antisite and Zn interstitial are associated with emission in the visible region. The band edge transition peak is prominent in PL spectra. The ZnO quantum dots exhibit strong UV emissions at 3.20eV and 3.16eV while other emissions in the range 3.00eV -- 1.77eV for the prepared samples.

Keywords: Polyvinyl alcohol, photoluminescence, De-convolution.

Introduction

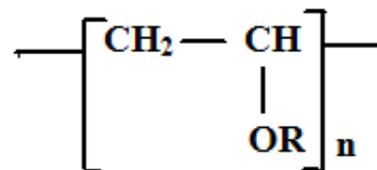
Zinc oxide is a versatile material which is used extensively in the field of nanoscience research. Its unique property of having high melting point, wide band gap (3.37eV), large exciton binding energy (60meV), etc. is making it suitable for its wider applications^{1,2}. The properties of nanomaterials being different from that of bulk in having larger surface to volume ratio, quantum confinement effect, etc. are drawing increasing research interest. Consequently ZnO nanostructure based LEDs, photo detectors, nano generators are emerging as potential ZnO based nanodevices.

Photoluminescence (PL) investigations yield information on the optical properties and the quality of synthesized material. In photoluminescence, particle absorbs photons and then re-radiates photons. Photo excitation of a bulk semiconductor creates exciton, bound by weak columbic interaction. The minimum energy required to generate such an exciton is called the band gap energy. The increase of energy difference between energy states and band gap is due to quantum confinement effect. Spectrum of UV and visible band emissions are observed in ZnO nanoparticles. The recombination between electrons in the conduction band and holes in the valence band causes UV emission³. Mid-band gap states are present in the defects of the crystal lattice of the ZnO. The donors and acceptors are the cause for the defect luminescence in ZnO lying in the visible spectrum. The types of defects can be recognised from the wavelength of the emission spectrum. Oxygen vacancy and Zn interstitial are the type of defects that result into visible emission. So far the quality of the prepared material is concerned, the intensity of the PL spectra provides the necessary information^{4,5}. Various methods have been applied till date to investigate the origin of the defects in the emission spectra of

nano ZnO but controversies remain till today^{6,7}. In order to study the defect centers, the PL spectrum of ZnO nanoparticle was deconvoluted by Gaussian fitting. The schematic energy levels for ZnO nanostructures treated with and without H₂O₂ are estimated. The treatment of ZnO with H₂O₂ may decrease the content of surface oxygen vacancies as reported by other workers and also this carries the potentiality of endowing better electrical properties to ZnO.

Material and Methods

Synthesis: Chemical bath deposition (CBD) method was employed for necessary synthesis^{8,9}. A 3% Polyvinyl Alcohol (PVA) solution was added into the salt solution of zinc sulphate (ZnSO₄) and sodium hydroxide (NaOH) prior to mixing for the necessary capping effect. The temperature of mixture solution was raised to 353K and kept under constant stirring using magnetic stirrer for 3hours to facilitate the reduction reaction to form ZnO nanostructures (sample-1)¹⁰. To the milky white solution of ZnO nanoparticles formed, an additional hydrogen peroxide (H₂O₂) solution (30%) was added. The resultant colloidal solution was then again put under constant stirring at high temperature for another 1 hour and then collected after cooling to RT(sample 2). Zinc oxide (ZnO) nanostructures were dispersed in presence of (PVA) matrix. The structure of polyvinyl alcohol (partially hydrolysed) is shown below.



Where R = H or COCH₃: Polyvinyl alcohol is produced from polyvinyl acetate. The two factors i.e. polymerisation and hydrolysis influence its applications. The agglomeration of the nanoparticles is prohibited by PVA. Besides it also acts as a coating agent¹¹. Polymers can act as a good stabilizing agent for they can cover a larger surface area of the nanoparticle¹². Studies reveal that nano crystal of suitable size can be obtained by optimizing capping agent concentration during the growth process.

Characterization: JEM -2100, a high resolution transmission electron microscope (HRTEM) helps revealing the morphology of nanoparticles and their sizes in detail. It has resolution of 1nm or less. Here the transmitted and diffracted electrons generate two dimensional projection of the sample. On viewing at high magnification, contrast in the image is observed in the form of periodic fringes which is referred to as phase contrast. PL of the as-prepared samples were investigated using a He-Cd laser, a 1m Cerny-Turner spectrograph, and a photomultiplier tube [Thermospectronics, Model: AB2 (Aminco Bowman Series 2)]. and thereby the luminescent properties of the nanoparticles were characterised. Optical transitions were investigated for the as-prepared samples using excitation wavelength of 325nm. Deconvolution of the PL spectra was done using the software version of OriginPro 7.0. PL data imported into Origin are being deconvoluted using Gaussian function.

Results and Discussion

The formation of large number of spherical ZnO quantum dots of average sizes 5.77nm have been confirmed by TEM images. In addition, the HRTEM shows the prime lattice spacing obtained in the range 0.22nm which is close to the (002) plane d-spacing of hexagonal ZnO.

Figure-1(a) shows the ZnO quantum dots in PVA matrix along with the bigger nanoparticles of ZnO. The outer layers of these bigger nanoparticles contain zinc peroxide (ZnO₂). This type of formation of zinc peroxides over zinc oxide was also reported by other workers. In the HRTEM image of figure-1(b) the

lattice fringes are seen. Thus the nanoparticles formed are crystalline in nature. The selected area electron diffraction (SAED) pattern is used to learn about the crystalline property of the sample. The SAED pattern of single crystalline material has only spot pattern while polycrystalline material has the form of ring pattern¹³. The figure-1(c) shows SAED pattern of the ZnO nanocrystal clearly corresponding to a single crystalline with some degree of disorder as evident by spot formation instead of rings.

UV-Visible spectroscopy on the synthesized product yielded exciton peak (not shown here) at 293nm. The band gap is estimated to be 4.24eV which is 0.87eV higher than that of bulk ZnO thereby indicating blue shifting¹⁴.

The nanosized ZnO synthesized in aqueous medium was dispersed in PVA matrix and the corresponding photoluminescence spectra were obtained using the excitation wavelength of 325nm which is shown in figure-2. Due to the size effect the PL peak position of sample 2 is located at 355nm while that for sample 1 is located at 361nm. From bulk ZnO to nanocrystal of ZnO there is observed increase in the intensity of UV peak. Further increase in intensity of UV peaks is found because of the formation quantum dots of ZnO nanoparticle¹⁵. The sample 1 shows an emission maximum at 396nm along with others at 360nm and 470nm. The UV emission found at 396nm is due to excitonic recombination corresponding to near band -gap emission. On the other hand oxygen vacancies result into blue emission at 470nm. The desorption of oxygen on the surface of ZnO nanoparticles may cause the enhancement of PL intensity. The electron-hole pairs recombine nonradiatively because the interstitial oxygen ions (O_i⁻ and O_i²⁻) reacting with H₂O₂ provide surface states to trap photo generated holes. On oxygen being removed from the surface of the ZnO nanoparticles, fewer centers of nonradiative recombination lead to an increase in PL intensity¹⁶. The ZnO quantum dots exhibit strong UV emissions at 3.13eV and 3.18eV while near blue emission at 3.66eV for the prepared samples.

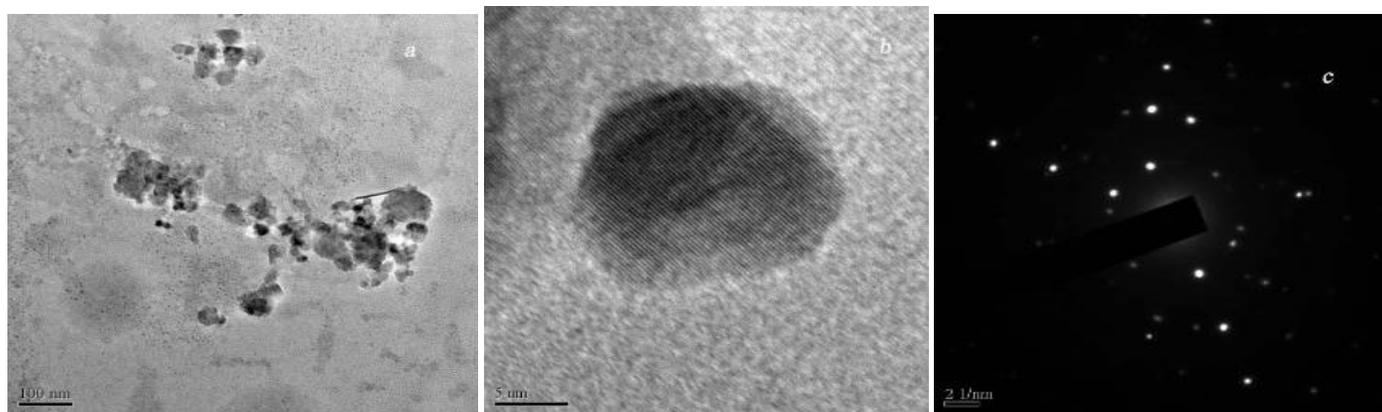


Figure-1

HRTEM images of (a) ZnO quantum dots and ZnO nanocrystals and (b) lattice spacing of nano ZnO in the background of PVA matrix (c) a SAED pattern of ZnO nanocrystal

The structural defects like oxygen vacancy, Zn interstitial or impurity may result into deep-level emissions¹⁷. In our case here, the emission in the visible region may also be attributable to the ZnO₂ formation. There is blue-green emission of ZnO at interstitial sites that results from the transition with a self activated center^{18, 19}. The self activated centers are formed by a doubly -ionized Zn vacancy V_{zn}²⁻ and the singly ionized interstitial Zn. The recombination of electrons in oxygen vacancies also leads to green emission band in the sample. The singly ionized oxygen vacancy in ZnO causes weak green band emission. The corresponding emission is due to the recombination of a photogenerated hole with the singly ionized charge state of the particular defect²⁰. The cause of yellow

emissions may be due to the radiative recombination of photo-generated holes and electrons in the singly or doubly ionized oxygen interstitials (O_i^{-/2-}) and oxygen anti-sites (O_{zn}^{0/-})²¹. Red luminescence band is attributed to doubly ionized oxygen vacancies.

In the PL spectra intense band edge transition peaks are seen while the sub-band transition peaks are found to be suppressed and diffused. Majority workers found UV excitonic absorption and emission in ZnO nanostructures which yielded additional emissions in the blue-green-yellow regions attributing the defects in the samples correspond to the growth conditions²².

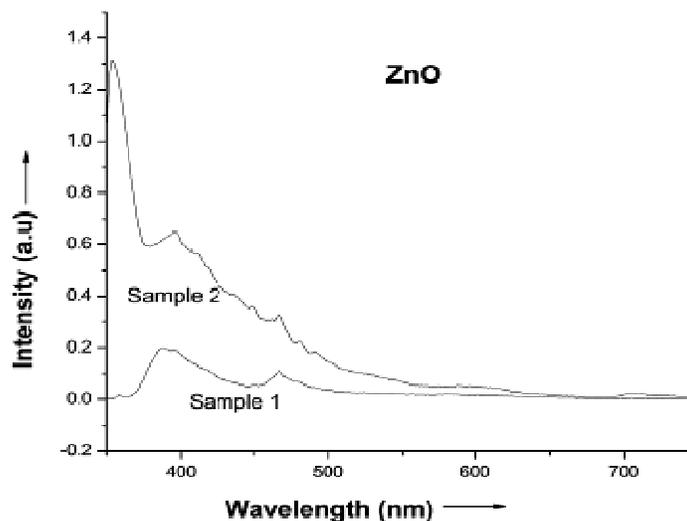


Figure-2
 PL spectra of ZnO (sample 1) and H₂O₂ treated ZnO (sample 2)

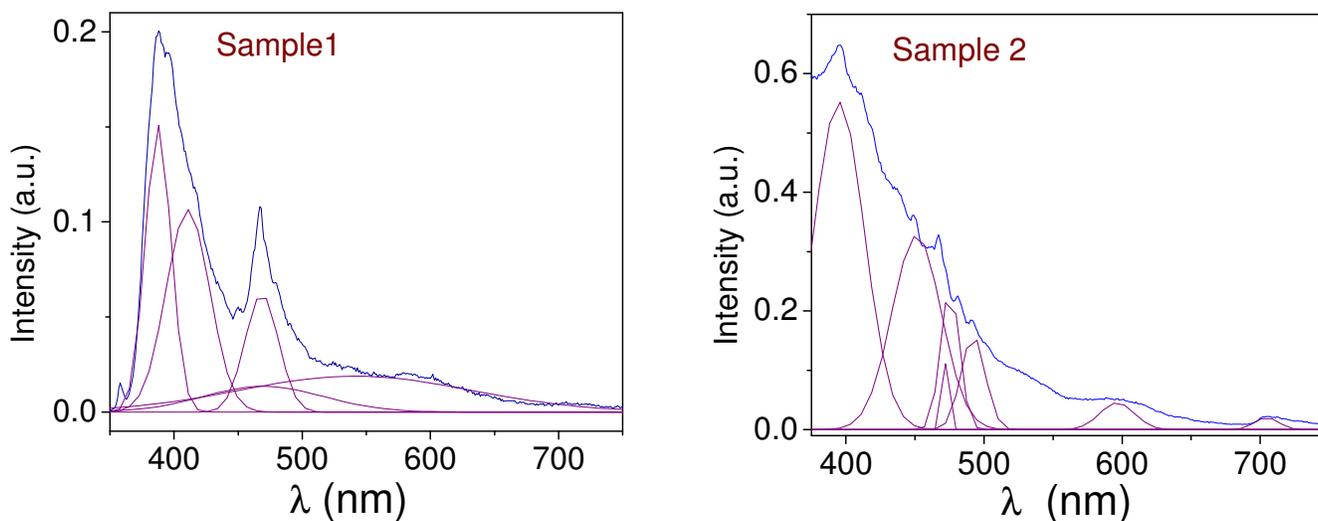


Figure-3
 Deconvolution of the Photoluminescence peaks (a) without H₂O₂ and (b) with H₂O₂ treated ZnO nano particles

The PL spectrum obtained for the samples was de-convoluted using Gaussian function as indicated in figure- 3(a-b). The peak positions help to find the energy levels of the intrinsic defects²³. The PL peaks for the H₂O₂ treated ZnO was de-convoluted into five peaks centered at ~ 394, 449, 498, 593 and 703nm respectively, whereas for sole ZnO nanoparticles, the PL peaks was de-convoluted into four peaks at~ 388, 414, 466 and 573nm respectively. Other workers such as Kim *et al* reported broad and intense PL peak at 414.6 nm in ZnO quantum dots while Liu *et al* observed it in bulk ZnO. These features are attributed to the existence of point defects. According to Wei *et al* the corresponding band is due to radiative transition of electrons from shallow donor levels which is created by oxygen vacancies to the valence band²⁴.

The deconvolution of the PL peaks was done employing Gaussian curve fitting. Table-1 displays the peaks of the individual components along with the corresponding estimated energy levels.

Nanocrystals grown by chemical methods have many defects. The defects in the crystal lattice of the ZnO, in the mid-band gap states are due to either a donor or an acceptor. The defect level emissions are found in the PL spectra. The higher crystalline quality of the ZnO crystal is ensured by the weaker emission in the visible region. Emission peaks at the UV region corresponding to near band edge (NBE) emission and visible emissions at violet and blue corresponding to shallow level emissions (SLE) and at green and red corresponding to deep level emissions (DLE) were found.

Table-1
PL peak positions and energy levels in the sample

Peak Nos.	Sample no.1 (Only ZnO)		Sample no.2 (H ₂ O ₂ treated ZnO)	
	λ(nm)	Energy (eV)	λ(nm)	Energy (eV)
I	388	3.20	394	3.16
II	414	3.00	449	2.77
III	466	2.67	498	2.50
IV	573	2.17	593	2.10
V	-	-	703	1.77

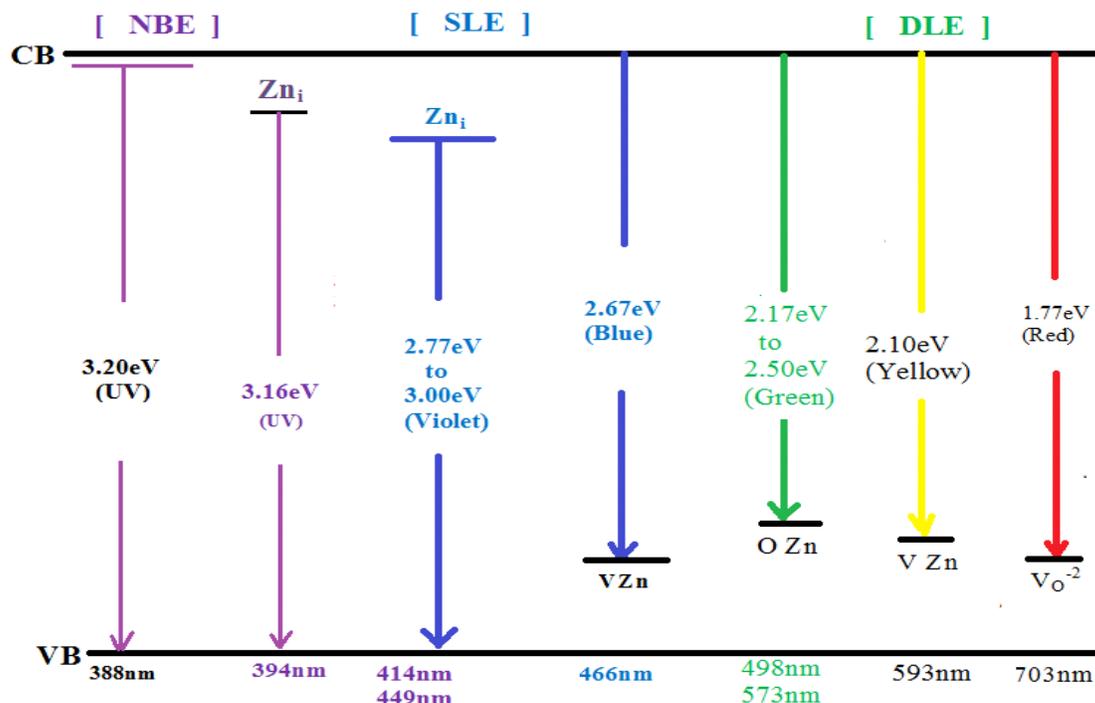


Figure-4

Schematic energy level diagram illustrating the emission mechanism from ZnO nanoparticles where V₀ is oxygen vacancy and V_{zn} is zinc vacancy and O_{zn} antisite oxygen

From the observed photoluminescence spectra, the schematic energy level diagram of ZnO nanoparticles is depicted as shown in figure-4. From the comparison of the peak wavelengths of the two samples red shift can be noticed. Thus after being treated ZnO with H₂O₂ red shifting occurred which is evident from the de-convolution of the photoluminescence peaks of the two samples.

Conclusion

The photoluminescence spectra exhibit Strong emission peaks around 360-396 nm. The red shifting in the PL spectra is clearly reflected from the de-convolution of the photoluminescence peaks of the two samples. The reason for this is the addition of hydrogen peroxide (H₂O₂) solution to the solution of ZnO nanoparticles. The peak positions obtained after de-convolution help in finding the energy levels of the intrinsic defects. Additional small blue-green-orange emissions were also found which are attributed to the inherent native defects created in the samples. The emission in the visible region may also be attributable to the ZnO₂ formation. The emission spectra of photoluminescence are observed to be high-intensity in UV range and very low intensity in the visible range. Thus a good surface morphology of the ZnO nanoparticles with minimum of surface defects is being established in our observation.

Acknowledgements

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